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Electronic Structure from Iron L-edge Spectroscopy: An Example of Spin Transition Evidenced by Soft X-ray Absorption Spectroscopy

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Abstract

Soft X-ray Absorption Spectroscopy at the transition metal $L_{2,3}$ edges provides information about the 3d unoccupied states by dipole allowed transitions. We have recorded iron $L_{2,3}$ edges in order to follow the reversible thermal spin interconversion (S=2 <---> S=0) of the Fe(II)(o-phenantroline)$_2$(NCS)$_2$. Huge differences are observed which demonstrate that the $L_{2,3}$ metal edges are a good fingerprint of the spin state and can be used to evidence an interconversion of the spin state.

Introduction

The electronic structure of 3d transition metal compounds is strongly modified by the filling of the 3d states. $L_{2,3}$ absorption spectroscopy is a fundamental probe of the empty 3d states because of the restrictive electric dipole selection rules.The configuration of the 3d valence states in iron compounds is influenced by the oxidation state as well as by the local environment (symmetry, nature of the ligand and metal-ligand distances) : the role of these parameters have been previously investigated [1-2]. Another important parameter is the spin state which depends mainly on the chemical environment and which involves directly the d levels[3].

Spin transition in Fe(II)(o-phenantroline)$_2$(NCS)$_2$

In a few number of transition metal molecular compounds, the ligand field strength is of the same order of magnitude as the average electron pairing energy. The metal ion is then capable of undergoing a spin state interconversion under the effect of an external perturbation such as a temperature change. Compounds that present this kind of reversible spin transition could be useful for electronic devices (switching, signal processing, data storage).

We report a reversible spin transition, studied and thermocontrolled "in-situ" of Fe(II)(o-phenantroline)$_2$(NCS)$_2$. This compound crystallises in an O_h symmetry. In such an octahedral environment, the 5-fold degenerated 3d-orbitals are divided into two distinct representations of T_{2g} and E_g symmetry with three and twofold degeneracy respectively. The Fe(II)(o-phenantroline)$_2$(NCS)$_2$ presents an abrupt and reversible spin transition $t_{2g}^4e_g^2$[S=2]---> $t_{2g}^6e_g^0$[S=0] which is complete at T=170K. In the high spin ground state - and for an octahedral environment-, the higher lying orbitals are occupied with the spins oriented in the same direction ($t_{2g}^4e_g^2$ configuration), while in the low spin ground state, the electrons pair up in the orbitals with the lowest energy ($t_{2g}^6e_g^0$ configuration).We have measured the variation of the magnetic susceptibility as a function of temperature. The result is shown in figure 1 and gives a good indication for a complete high/low spin interconversion S=2 <---> S=0 at T = 176K.

During the spin transition, the space group (*Pbcn*) remains unchanged : the arrangement of the Fe(II)(o-phenantroline)$_2$(NCS)$_2$ units is quite the same in the high and low-spin forms[5]. At low temperature, the more noticeable intramolecular modifications associated with the spin transition are those that affect the geometry of [FeN_6] group[5-6]. The high-spin / low-spin conversion is characterized by a shortening of the Fe-N distances [ΔR = 0.20 Å for the Fe-N(phen) bonds and 0.10 Å for the Fe-N(CS) bonds].

Results and discussion

L-edge spectra were recorded in electron yield mode with beam line U4-B [4] at the National Synchrotron Light Source. We have

recorded iron L-edge spectra above and below 170K. For the measurements at 77K, the sample temperature was lowered at a rate of 2K/min to avoid a quenching of the spin state.

Figure 2 shows the Fe $L_{2,3}$ edges of the spin transition complex Fe(II)(o-phenantroline)$_2$(NCS)$_2$ recorded at 300K and 77K. There are huge differences between the two spectra : at 77K the whole spectrum is shifted to higher energies (1.44 eV for the L_3 maximum and 0.5 eV for the L_2) and the L_3 peak presents better resolved structures. The L_2 white line which presents three well resolved features at 300K becomes simplified at low temperature and increases strongly in intensity. We have observed in other iron compounds that such a shape for the L_2 peak is the signature of a low spin configuration.

Figure 3 compares the initial Fe $L_{2,3}$ spectrum to the one obtained after the full cycle, i.e. after cooling from 300K and heating again to room temperature, and evidences the complete reversibility of the spin transition.

The very important differences between the spectra corresponding to the two spin states reflect not only the modifications of the ground state configuration but also that of the final state. A comparison of our experimental spectra with the calculations of Ref. [7] enables us to estimate the value of the crystal field parameter in the high-spin state to be close to 0.5eV. However, no such calculation is available for the low-spin configuration.

Let us now turn our attention to the variation in relative intentity (Branching ratio) of the two L edges with the spin transition. At low temperature, where the spin state of the iron compound considered is S = 0, the spin orbit operator is equal to 0. Therefore the branching ratio amounts to the statistical value which is equal to 0.66 [8]. Calculating the respective areas of the L_2 and the L_3 peak in the 77K spectrum of Fe(II)(o-phenantroline)$_2$(NCS)$_2$, we obtain an experimental value for the branching ratio equal to 0.67, in very good agreement with the theory.

Experimentally, we computed from peak areas in the 300K spectrum a branching ratio of 0.79 for the S=2 spin state. The branching ratio for 3d metals has been calculated [8] for all configurations and all the J levels of the Hund's rule ground state LS terms within the free atom approximation, yielding a value of 0.78 for a d^6 (S=2, J=4) configuration.

The spin-orbit expectation value, computed from crystal-field theory, increases the branching ratio by 0.044. Hence, the experimental value falls between the two theoretical ones (with and without crystal field effect). This agreement appears fairly good, taking into account the uncertainty in the experimental determination of the branching ratio.

Conclusion

We have demonstrated that the $L_{2,3}$ transition metal edges are a good fingerprint of the spin state and can be used to evidence an interconversion between two different spin states.

Aknowlegments

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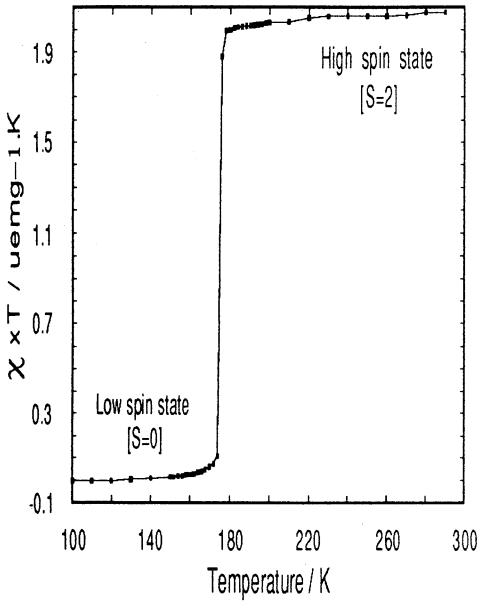

Figure 1: Temperature dependence of the χ_m.T for the Fe(phen)2(NCS)2 sample. (The magnetic susceptibility measurements were performed over the temperature range 295-77 K, by using a Faraday type magnetometer equipped with a continuous-flow cryostat.)

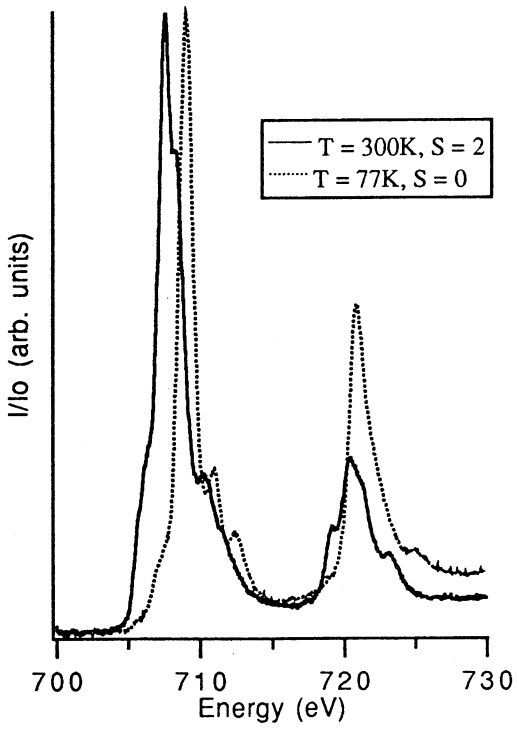

Figure 2 : Experimental $L_{2,3}$ absorption spectra of Fe(phen)2(NCS)2 at :
(a) 300K (high spin configuration S = 2)
(b) 77K (low spin configuration S = 0)

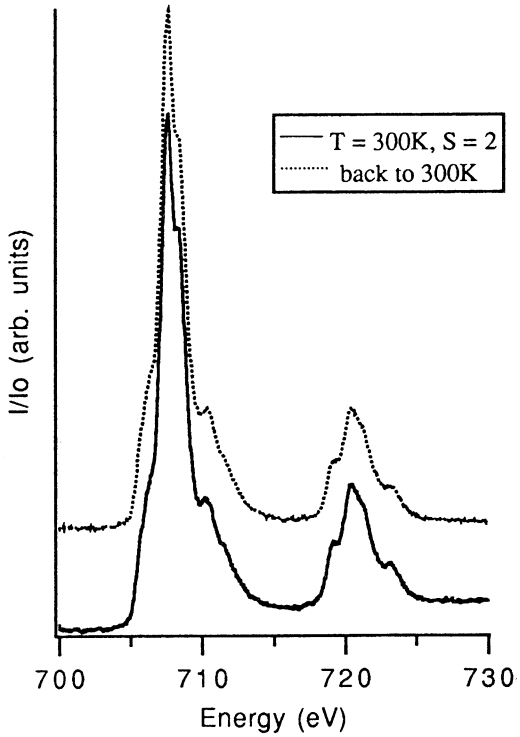

Figure 3 : Comparison of the $L_{2,3}$ absorption spectra of Fe(phen)2(NCS)2 at 300 K **(a)** before and **(b)** after the spin transition.